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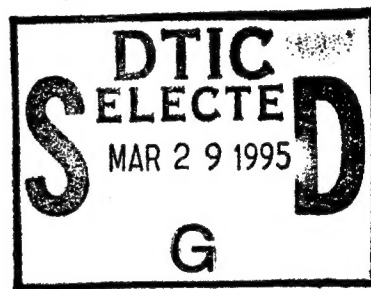
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INVESTIGATION OF ANOMALOUS PREDICTED BOND LENGTHS IN SOME 1,1-DIFLUOROHYDRAZINES

Peter Politzer* and M. Edward Grice

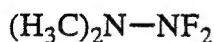
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Abstract

Bond length anomalies found in some 1,1-difluorohydrazines are conformation-dependent and are absent in the presence of strongly electron-attracting substituents, supporting their interpretation in terms of charge delocalization.

Introduction

In a recent computational study of the 1,1-difluorohydrazines **1** - **3**,¹ our optimized ground state geometries revealed the interesting features that (a) one N-F bond is considerably longer than the other, and (b) the N-N distances are shorter than anticipated. The relevant data are summarized in Table 1; they were obtained by a density functional procedure using the Gaussian 92/DFT code,² with the Becke exchange³ and Perdew correlation⁴ functionals and a 6-31G** basis set. It was verified, by the absence of negative vibration frequencies, that these geometries correspond to local energy minima.⁵ Also included in Table 1, for reference purposes, are computed bond lengths for $\text{H}_3\text{C}-\text{NF}_2$ and $(\text{H}_3\text{C})_2\text{N}-\text{NH}_2$. These shall be viewed as being reasonably typical values for these bonds, within the framework of the computational approach.



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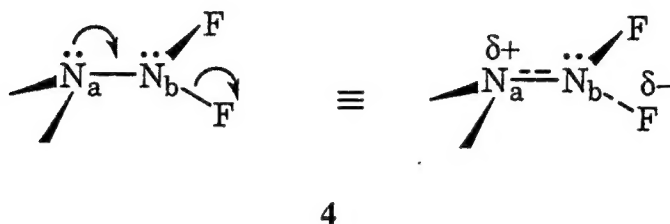
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In the molecules **1** - **3**, one N-F bond has a length very similar to those in $\text{H}_3\text{C}-\text{NF}_2$, while the other is at least 0.1 Å longer. On the other hand, the N-NF₂ bonds are more than 0.1 Å shorter than in $(\text{H}_3\text{C})_2\text{N}-\text{NH}_2$. We suggested in our earlier paper that these features reflect a delocalization of electronic charge such as is depicted in **4**:¹



This delocalization, which can be viewed as an example of the anomeric effect,⁵⁻⁸ is presumably most effective if the lone pair on N_a is concentrated in the same plane as the N-N and one of the N-F bonds; thus one of the latter is lengthened but not the other. (An extended discussion of the nitrogen lone pairs in some 1,1-dimethylhydrazines has been presented by Murray *et al.*⁹)

Results and Discussion

In an effort to better understand the electronic and structural factors in these molecules, we investigated the effects of rotating the NF₂ portion of **1** around the N-N bond. Using the computational procedure described above, the geometry was re-optimized at 60° intervals relative to the completely eclipsed conformation, **1A**. On this basis, the ground state, **1C**, corresponds to a rotation of 69.9°. The results are shown in Figure 1.

The most striking situations are found in **1B** and **1D**. In **1B**, the lone pair on N_a is exactly coplanar with the N-F_a bond. The latter is consequently greatly elongated, to 1.564 Å, while the N-F_b is a normal 1.422 Å. In **1D**, after a rotation of 60°, the lone pair of N_a is coplanar with the N-F_b bond, and now the latter is the one that is anomalously long, 1.505 Å, and the N-F_a is normal, at 1.432 Å. In both conformations, the N-N bond is considerably shortened, to the 1.36 Å - 1.38 Å range; this is about 0.12 Å less than in $(\text{H}_3\text{C})_2\text{N}-\text{NH}_2$. The computed ground state, **1C**, is quite similar to **1B**.

In **1A** and in **1E**, on the other hand, the lone pair on N_a affects both N–F bonds equally; thus both have the same length. The N–F and the N–N distances in **1A** and **1E** are all intermediate between their extreme values in **1B** and **1D** and their normal ones in H_3C-NF_2 and $(H_3C)_2N-NH_2$. This indicates that some delocalization of charge is occurring, but not to the same extent as when the N_a lone pair is coplanar with an N–F bond.

As would be anticipated, the highest energy conformation is **1A**, in which the two lone pairs eclipse each other. The completely staggered (*anti*) conformation **1E**, in which the lone pairs are at their maximum separation, is higher in energy than either **1B** (*gauche*) or **1D**; this presumably reflects the greater degrees of delocalization in the latter two, and the resulting stabilization.

The results presented in Figure 1 are consistent with the charge delocalization depicted in structure **4**, which is proposed as an interpretation of the bond length anomalies observed in **1** - **3**. While we have shown that these molecules do have energy minima, the presence of the elongated N–F bond in each of them reinforces concern regarding a possible facile loss of fluoride ion.¹⁰ This could be a source of difficulties in synthesis. It was suggested by Baum¹¹ that this problem could perhaps be avoided or diminished by having electron-attracting substituents on N_a , which would have the effect of opposing the charge delocalization shown in **4**.

We have accordingly investigated the structure of $(NC)_2N-NF_2$, in which two cyano groups have been substituted on N_a ; these are known to be strongly electron-withdrawing through induction.¹² The geometry was optimized at the Gaussian 92/DFT/B-P86/6-31G** level, and was verified to correspond to an energy minimum. The consequences of introducing the cyano groups are quite pronounced. The bonds around N_a become essentially coplanar, in contrast to their distinctly pyramidal arrangements in **1** - **3**. The N–F bond lengths are now nearly the same and are quite normal, 1.410 Å and 1.420 Å, as is the N–N, 1.460 Å (Table 1). Thus the anomalies found in **1** - **3** have been eliminated; the anomeric effect is not observed in $(NC)_2N-NF_2$.

These findings provide further support for our interpretation of these anomalies in terms of

4. They also offer some encouragement concerning the feasibility of synthesizing compounds of the type $R_aR_bN-NF_2$, in which R_a and R_b are strongly electron-attracting.

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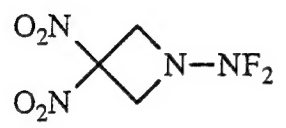
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Table 1. Computed bond lengths.^a

Molecule		Bond	Length (Å)
(H ₃ C) ₂ N—NF ₂	1	N—F	1.431, 1.542
		N—N	1.358
	2	N—F	1.418, 1.536
		N—NF ₂	1.368
	3	N—F	1.417, 1.538
		N—N	1.366
H ₃ C—NF ₂		N—F	1.436, 1.436
(H ₃ C) ₂ N—NH ₂		N—N	1.492
(NC) ₂ N—NF ₂		N—F	1.410, 1.420
		N—N	1.460

^aReference 1; obtained by density functional Gaussian 92/DFT/B-P86/6-31G** calculations.

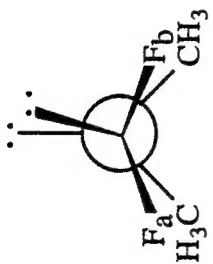
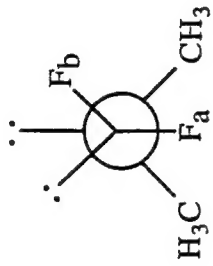
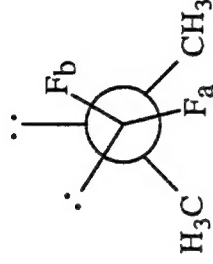
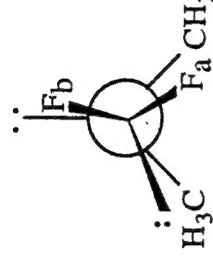
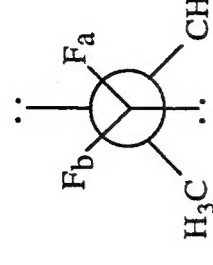
					
Angle of rotation (deg)	0	60	69.9	120	180
Relative energy (kcal/mole)	13.1	0.4	0.0	7.9	8.9
N-F _a length, Å	1.493	1.564	1.542	1.432	1.464
N-F _b length, Å	1.493	1.422	1.431	1.505	1.464
N-N length, Å	1.421	1.362	1.358	1.376	1.423

Figure 1. Calculated properties of conformers of $(\text{H}_3\text{C})_2\text{N}-\text{NF}_2$ produced by rotation around N-N bond. The lone pairs on the two nitrogens are included in the Newman projections. **1A** and **1D** represent completely eclipsed conformations; **1C** is the ground state.